Implementing the Shockley-Queisser efficiency limit in SCAPS

Marc Burgelman
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Correspondence address: Dept. of Electronics and Information Technology (ELIS),
University of Gent, 'Belgium'.
E-mail: Marc.Burgelman@ugent.be

1. Introduction

The SCAPS application discussed in this document uses:

- SCAPS version 3.3.11 of September 2023, or more recent.
- the definition file `simple pn S-Q.def`

2. What is the problem?

It can happen – and it did happen! – that a SCAPS user simulates a solar cell and obtains unrealistic, even straight out unphysical high efficiency parameters. It can even happen with a very simple problem, e.g. with `simple pn.def` from the SCAPS distribution.

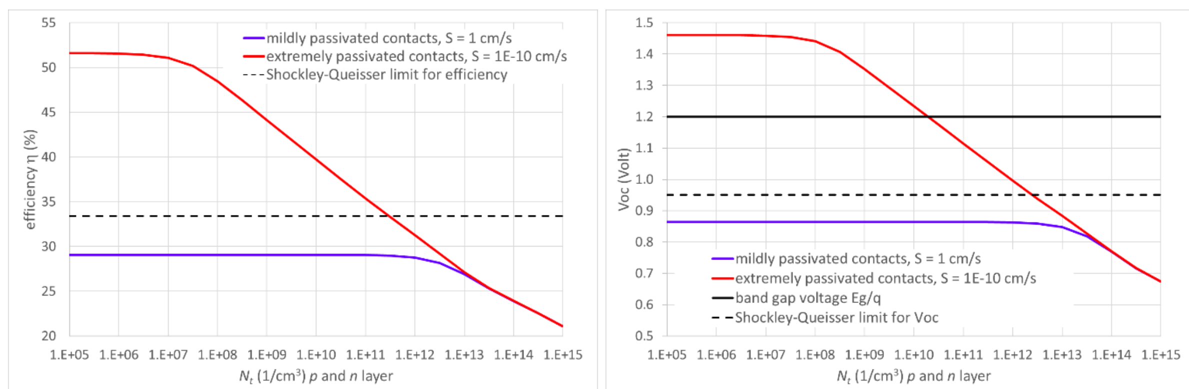

Fig. 1 Left: efficiency η and Right: open circuit voltage V_{oc} simulated by SCAPS for the problem file `simple pn.def`. The defect density N_t was varied simultaneously in the *p* layer and in the *n* layer, from extremely low (10^5 cm^{-3}) to rather high (10^{15} cm^{-3}). Blue: with a well passivated contact front and back (S = 1 cm/s). Red: with an extremely well passivated contact ($S = 10^{-10}$ cm/s). The Shockley-Queisser limits for efficiency η and for open circuit voltage V_{oc} are indicated, as well as the voltage corresponding to the band gap E_g = 1.2 eV of the *p* and *n* layer.

With the other settings of `simple pn.def`, the efficiency parameters are high, but not directly alarmingly high, as is illustrated the blue curves of Fig. 1 for the efficiency η and the open circuit voltage V_{oc}. But when we set the surface recombination at the contacts extremely low, $S_n = 10^{-10}$ cm/s at the *p*-contact, and , $S_p = 10^{-10}$ cm/s at the *n*-contact, the user should be alarmed, as seen from the red curves in Fig. 1: the V_{oc} value gets unphysically high, even above the band gap voltage! And also, both η and V_{oc} are clearly above their Shockley-

Queisser limit for the band gap value E_g = 1.2 eV (Most SCAPS users are aware of the concept of the Shockley-Queisser limit; it will be explained later on).

So we must conclude: SCAPS can calculate efficiencies η above the theoretical efficiency limit η_{SQ} of Shockley and Queisser… because a user can define unphysical parameter values!

Here, the culprit clearly is the low recombination: for the red curves in 1, there is as good as no surface recombination at the contacts; there was no interface recombination defined; in both layers, two recombination mechanisms were set rigorously to zero (band-to-band recombination and Auger recombination); thus, the only recombination present is in the defect in the semiconductor layers. Clearly, when the defect density N_t is lower than about 10^{10} to 10^{11} cm^{-3}, the total recombination is unphysically low, giving unphysically high values for η and for V_{oc}.

Most recombination mechanisms present in (the SCAPS model of) a solar cell do not have physical lower limit, however, one single mechanism has!

1. Surface recombination at the contacts: An experimentalist would consider a contact with S = 1 cm/s as very, very well passivated. However, there is (to my knowledge) no physical argument against much lower values of S, even $S = 0$.

2. Interface recombination between two semiconductor layers: there is (to my knowledge) no physical argument against very low values of N_i, the density of interface states, so there is no physics that would prevent a SCAPS user to set $N_i = 0$ (making such an ideal interface in practice could be very difficult/impossible, however).

3. SCAPS implements three recombination mechanisms in a (semiconductor) layer:

    1. Shockley-Read-Hall (SRH) recombination describes recombination of electrons and holes via a defect state. The recombination rate through this mechanism is proportional to the defect density N_t. There is (to my knowledge) no physical argument against very low values of N_t, so there is no physics that would prevent a SCAPS user to set $N_t = 0$ (making such an ideal semiconductor layer in practice could be very difficult/impossible, however; perovskite researchers claim that their materials are performing very well in this respect).
    2. Auger recombination describes the interaction between two conduction band electrons and one valence band hole (or two holes and one electron). The mechanism is described with two Auger constants C_n and C_p. There is (to my knowledge) no physical argument against very low values of C_n and C_p, so there is no physics that would prevent a SCAPS user to set $C_n = C_p = 0$.
    3. Band-to-band recombination, describing the direct recombination of a conduction band electron with a valence band hole. When light is emitted in this process (thus emission of a photon), the mechanism is also called *radiative* recombination. It is described by a recombination constant C_r (r of radiative)… and there is a physical lower limit to recombination via this mechanism: the famous Shockley-Queisser limit, that is further discussed below. In most practical materials, SRH recombination will dominate, and setting an appropriate value to the band-to-band recombination will not be relevant. For this reason (and because an appropriate value of C_r is difficult to find for most materials that are considered for photovoltaics), the default value of C_r in SCAPS is zero (as it also is for the Auger mechanism $C_n = C_p = 0$),

… thus, when a user leaves the default settings for band-to-band and Auger recombination, and sets very low values for the other recombination mechanisms (contacts, interfaces, SRH), a “Shockley-Queisser accident” can happen in SCAPS!

3. The Shockley-Queisser efficiency limit of a solar cell

The original paper by Shockley and Queisser was published in 1961 [1]. The subject got renewed interest, and was further elaborated in the early 80-ties, e.g. [2][3]. These historical articles might be difficult to get at nowadays. Fortunately the subject is regularly retaken in more recent text books that could be more readily available, e.g. [4][5][6]. And – even more fortunately – decent information can also be found on Wiki [7].

The starting point is the idealised *IV* law of a single-junction solar cell

$$J(V) = J_0\left[\exp\left(\frac{qV}{kT}\right) - 1\right] - J_L \qquad (1)$$

where J_0 is the dark current (density) and J_L the light current (density), T is the ambient temperature, V the voltage over the cell, q the elementary charge and k the Boltzmann constant. Shockley and Queisser [1] pointed out that the dark current J_0 cannot be arbitrary low, but has a physical lower limit. They argue that a cell in the dark is in fact surrounded by a black body (BB) at temperature T. This black body surrounding emits radiation, according to Planck's law, to the cell. The cell absorbs the black body photons with energy above the bandgap of the solar cell material, that are generating electron-hole (*eh*) pairs. Those *eh* pairs then recombine (re-emitting photons with the band gap energy). In equilibrium (dark; no voltage $V = 0$), these two mechanisms – absorbing BB photons and re-emitting them by recombination – must balance each other. That is the 'detailed balance principle'. Since a cell necessarily has a surrounding, that is always at a temperature $T > 0$, there is always BB radiation coming in from the surrounding, and thus always an equal amount of recombination: it cannot be avoided, and hence this constitutes the physical lower limit of recombination.

The dark current associated with this black body radiation from the surrounding is found to be:

$$J_0 = \frac{2\pi q}{c^2}\int_{\nu_g}^{\infty} \nu^2 \frac{1}{\exp\left(\frac{h\nu}{kT}\right) - 1} d\nu \qquad (2)$$

where c is the velocity of light, ν the frequency of the photon and h the Planck constant. The photon energy is given below:

photon energy $= h\nu$ thus for a photon with energy equal to the band gap: $h\nu_g = E_g$ (3)

The integration in Eq. (2) is thus for all photons with energy above the band gap E_g. Equation (1) and (2) imply that under forward bias ($V \gg kT/q$), the voltage dependence of the dark current is

$$J_{\text{forward}}(V) = J_0 \exp\left(\frac{qV}{kT}\right) = \frac{2\pi q}{c^2}\int_{\nu_g}^{\infty} \nu^2 \frac{\exp\left(\frac{qV}{kT}\right)}{\exp\left(\frac{h\nu}{kT}\right) - 1} d\nu \qquad (4)$$

A more careful derivation has shown that a better expression for the *V*-dependence of the dark current is [2][7]:

$$J_{\text{forward, corr.}}(V)=\frac{2\pi q}{c^2}\int_{\nu_g}^{\infty}\nu^2\frac{1}{\exp\left(\frac{h\nu-qV}{kT}\right)-1}d\nu \qquad (5)$$

It is easily shown that in most practical cases the error is negligible when we work with the simpler form (4) instead of the more rigorous form (5).

The Shockley-Queisser theory thus concludes that

- the recombination cannot become arbitrary low ($J_0 \rightarrow 0$), but that there is a minimum value imposed by the balance between recombination and incoming black body radiation from the ambient at temperature T, given by Eq. (4) or (5).

To derive maximum values for the efficiency parameters from that, Shockley and Queisser use some approximations/idealisations to calculate the light current J_L, and then, together with J_0 and the solar cell equation (1), the efficiency parameters. (Some of) these idealisations are:

- the solar cell has infinite thickness
- and thus absorbs all incoming light
- the absorption coefficient $\alpha(\lambda)$ of the solar cell semiconductor is a step function: α = a constant value α_0 for photon energy $h\nu > E_g$, and zero, thus $\alpha = 0$, for $h\nu < E_g$. And also that "α_0 is large enough"
- all absorbed photons give rise to one *eh* pair
- and all generated *eh* are collected at the contacts
- the two above assumptions are sometimes phrased as "the collection efficiency is unity (=1)", meaning that every incident photon contributes with one elementary charge q to the current.

SCAPS can do much better (and more realistic) than these coarse assumptions, and there is no need to implement one of these in SCAPS. When a user really wants to check the original Shockley-Queisser limit, she/he should chose the input parameters such that these assumptions are valid (thickness $d \gg$ the diffusion length(s), and $\gg$ the absorption depth $1/\alpha_0$; absorption model "step at E_g").

To ensure that the recombination is the minimum band-to-band recombination given by the Shockley-Queisser limit for J_0 , Eq. (4), one should

- set all recombination mechanisms to zero, or at least to a very low value so that band-to-band recombination (in the absorber, if it is a heterojunction) is the only, or at least the dominant mechanism. These mechanisms to be set 'very low' or straight-out zero are: recombination at the contacts (S_p at the *n*-contact, S_n at the *p*-contact); interface recombination (N_i at all interfaces), Auger recombination in the semiconductors (Auger constants C_n and C_p), defect recombination (SRH recombination) in all defects of all semiconductor layers (defect densities N_t).
- set the band-to-band (or 'radiative') recombination in the semiconductor layers to the Shockley-Queisser limit. The only parameter to be set is C_r, the radiative recombination constant.

… and that is an essential problem, since the Shockley-Queisser limit is defined as a surface property (thus, per unit surface of the solar cell; J_0 in Eq. (4) is in Acm^{-2} or Am^{-2}). And radiative recombination in SCAPS (and everywhere) is defined as a volume property (thus, per

unit volume of the solar cell; C_r is in $cm^{-3}s^{-1}$ or $m^{-3}s^{-1}$). This is because SCAPS solves the 'semiconductor equations' along the depth dimension x of the cell, and thus all inputs and outputs of SCAPS are functions of x. This x-dimension simply does not occur in the Shockley-Queisser theory, it is just assumed that the cell is infinitely, or at least 'sufficiently' thick.

So, we must first set-up a relation between the surface property J_0 and the volume property C_r. And then we must find suitable fast approximations for the result.

4. Relating the Shockley-Queisser J_0 to the radiative recombination constant Cr

The band-to-band recombination in SCAPS is given by

$$U_{\text{band-to-band}} \left(= U_{\text{radiative}}\right) = C_r \left(pn - n_i^2\right) \tag{6}$$

where p is the free hole density, n the free electron density and n_i the intrinsic carrier density. When only this recombination mechanism is present, we can define a life time τ and a diffusion length L for it. In the case of a p^+n cell with an n-type layer with thickness d (thickness of the neutral region, thus outside the depletion layer), and with uniform doping density N_A, one gets:

$$U = \frac{p - p_{n0}}{\tau_p} \quad \text{with} \quad \tau_p = \frac{1}{N_A C_r} \quad \text{and} \quad L_p = \sqrt{D_p \tau_p} \tag{7}$$

where D_p is the diffusion constant for holes in the n-layer, and p_{n0} is the equilibrium hole density in the n-layer. For this simplified problem, the dark current is given in many text books as:

$$J_0 = \frac{q n_i^2 D_p}{N_A L_p} \cdot \frac{\sinh\left(\frac{d}{L_p}\right) + \frac{S_p L_p}{D_p} \cosh\left(\frac{d}{L_p}\right)}{\cosh\left(\frac{d}{L_p}\right) + \frac{S_p L_p}{D_p} \sinh\left(\frac{d}{L_p}\right)} \tag{8}$$

When the n-contact is perfectly passivated, $S_p \to 0$ and the expression is greatly simplified to

$$J_0 = \frac{q n_i^2 D_p}{N_A L_p} \tanh\left(\frac{d}{L_p}\right) \tag{9}$$

(it is quicker, and a nice little exercise, to derive Eq. (9) directly, instead of searching for the 'full' solution (8) and then simplifying…). Considering that we are working at the Shockley-Queisser limit, the recombination will be very low (but not zero), thus the diffusion length will be very long (but not infinite), thus $d/L_p \to 0$, $\tanh(d/L_p) \to d/L_p$, and

$$J_0 = \frac{q n_i^2 D_p}{N_A L_p} \frac{d}{L_p} = \frac{q n_i^2 d}{N_A} \frac{D_p}{L_p^2} = \frac{q n_i^2 d}{N_A} \frac{D_p}{D_p \tau_p} = \frac{q n_i^2 d}{N_A} C_r N_A = q n_i^2 d \cdot C_r \tag{10}$$

(here we used Eq. (7)). This is an important relation between the surface property J_0 and the volume property C_r:

$$J_0 = q n_i^2 d \cdot C_r = q d N_V N_C \exp\left(-\frac{E_g}{kT}\right) \cdot C_r \tag{11}$$

where n_i has been expressed as a function of the effective density of states in conduction and valence band, N_C and N_V, in the familiar way. Remember the assumptions underlying the important Eq. (11): the *n*-contact is perfectly passivated, the diffusion length is long compared to the cell thickness; all recombination is in the quasi-neutral region of the *n*-layer, not in the depletion layer; and further all assumptions of the traditional Shockley diode theory.

This J_0 can be related to the Shockley-Queisser limit for J_0, that we call here $J_{0,\text{S-Q}}$; retaking Eq. (2) and (11):

$$J_{0,\text{S-Q}} = \frac{2\pi q}{c^2}\int_{\nu_g}^{\infty} \nu^2 \frac{1}{\exp\left(\frac{h\nu}{kT}\right)-1} d\nu = J_0 = qdN_V N_C \exp\left(-\frac{E_g}{kT}\right)\cdot C_r \tag{12}$$

Before discussing this expression for C_r in the Shockley-Queisser limit, we will simplify it.

5. Approximate expression for the radiative constant *Cr* in the S-Q limit

First, write all variables ν in the S-Q expression as the dimensionless parameter $z=h\nu/kT$ ($h\nu$ is the photon energy, kT the thermal energy):

$$\begin{aligned} J_{0,\text{S-Q}} &= \frac{2\pi q}{c^2}\left(\frac{kT}{h}\right)^2 \frac{kT}{h}\int_{\nu_g}^{\infty}\left(\frac{h\nu}{kT}\right)^2 \frac{1}{\exp\left(\frac{h\nu}{kT}\right)-1} d\left(\frac{h\nu}{kT}\right) \\ &= \frac{2\pi q}{c^2}\left(\frac{kT}{h}\right)^3 \int_{z_g}^{\infty} \frac{z^2}{\exp(z)-1} dz \quad \text{where} \quad z = \frac{h\nu}{kT} \text{ and } z_g = \frac{h\nu_g}{kT} = \frac{E_g}{kT} \end{aligned} \tag{13}$$

The integral can be evaluated analytically when $z_g \gg 1$:

$$\int \frac{z^2}{\exp(z)-1} dz \cong \int z^2 \exp(-z)\, dz = -\left(2+2z+z^2\right)\exp(-z) \tag{14}$$

yielding

$$\begin{aligned} \int_{z_g}^{\infty} \frac{z^2}{\exp(z)-1} dz &\cong \left(2+2z_g+z_g^2\right)\exp\left(-z_g\right) \\ &= \left(2+2\frac{E_g}{kT}+\left(\frac{E_g}{kT}\right)^2\right)\exp\left(-\frac{E_g}{kT}\right) \\ &\approx \left(\frac{E_g}{kT}\right)^2 \exp\left(-\frac{E_g}{kT}\right) \end{aligned} \tag{15}$$

The last approximation holds when $E_g/kT \gg 1$. In the range of interest, say 1 eV < E_g < 2 eV, and with $kT \cong 25$ mV at room temperature (300 K), the dimensionless parameter E_g/kT is in the range 40 to 80, and the error will be of the order of a few percent. We thus obtain from Eq. (13)

$$J_{0,\text{S-Q}} = \frac{2\pi q}{c^2}\left(\frac{kT}{h}\right)^2 \frac{kT}{h}\left(\frac{E_g}{kT}\right)^2 \exp\left(-\frac{E_g}{kT}\right)$$
$$= 2\pi cq\left(\frac{kT}{hc}\right)^3\left(\frac{E_g}{kT}\right)^2 \exp\left(-\frac{E_g}{kT}\right) \qquad (16)$$

This is a convenient expression: since we will express the thermal energy kT in eV, we can use the well known value of hc in convenient units:

$$hc = 1240\,\text{nm.eV} = 1.240\times10^{-4}\text{cm.eV} = 1.240\times10^{-6}\text{m.eV} \qquad (17)$$

(use the numerical value in cm×eV to obtain J_0 in A/cm^2 , and the value in m×eV to obtain J_0 in A/m^2). Now we only have to insert the approximated value of $J_{0,\text{ S-Q}}$ in Eq. (11) that relates Cr with $J_{0,\text{SQ}}$:

$$C_r = \frac{J_{0,\text{ S-Q}}}{qdN_V N_C \exp\left(-\frac{E_g}{kT}\right)}$$
$$= \frac{2\pi cq\left(\frac{kT}{hc}\right)^3\left(\frac{E_g}{kT}\right)^2 \exp\left(-\frac{E_g}{kT}\right)}{qdN_V N_C \exp\left(-\frac{E_g}{kT}\right)} \qquad (18)$$
$$C_r = \frac{2\pi c}{N_V N_C}\left(\frac{kT}{hc}\right)^3\left(\frac{E_g}{kT}\right)^2 \cdot \frac{1}{d}$$

This final equation is elegant. The only semiconductor properties involved are fundamental ones: the band gap E_g (that was expected!), and the density of states in conduction and valence band N_C and N_V… but the presence of the (absorber) layer thickness d could disappoint: the Shockley-Queisser limit is a fundamental physical property, so it is ‘ugly’ that we see a geometrical parameter, d , appear in Eq. (18) that must be used to implement S-Q in SCAPS. But, as said, when we must relate a surface property as J_0 to a volume property as Cr, we should not be surprised that a property with dimension [length] will appear. We are happy that no ’less fundamental’ properties appear, like doping density, mobility, diffusion constant… and with compassion with our old computer, that the exponential function exp(-qE_g/kT) has dropped out…

We checked the validity of Eq. (16) against the tabulated values of $J_0(E_g)$ in [6]. In the tabulated E_g range of 0.8 to 2.0 eV, the deviation of our approximation (16) is less than 6 %. This is largely sufficient, since a maximum deviation of 6% is expected to give a maximum deviation of V_{oc} of the order of $(kT/q)\ln(1.06) \cong 1.4$ mV.

6. Implementation of the Shockley-Queisser limit in SCAPS

… was done in SCAPS 3.3.11, September 2023.

Whether or not to take account of the Shockley-Queisser limit is set in the Numerical Panel, that is accessible from the orange button ‘Numerical settings’ in the Solar Cell Definition Panel. In the ‘recombination block’ bottom right of this panel, a new field is added, see Fig. 2.

1. The default is ‘Never set S-Q recombination limit’; then SCAPS works in the traditional way, and the user is free to use settings that violate the S-Q limit … and has the responsibility to remark this when it happens.
2. When ‘Always use the S-Q limit…’ is selected, SCAPS will calculate the band-to-band recombination constant that corresponds with the S-Q limit, $C_{r,\text{ S-Q}}$, using Eq. (18) above, and replace the user set C_r value with this $C_{r,\text{ S-Q}}$, regardless which of the two is the greater. The original user-set value of C_r is lost.
3. When ‘If recombination is too low, set it to S-Q limit’ is selected, SCAPS will calculate $C_{r,\text{ S-Q}}$ as above. It will leave C_r as is, if $C_r > C_{r,\text{ S-Q}}$, and it will replace C_r with $C_{r,\text{ S-Q}}$ if $C_r < C_{r,\text{ S-Q}}$; the original user-set value of C_r is then lost.

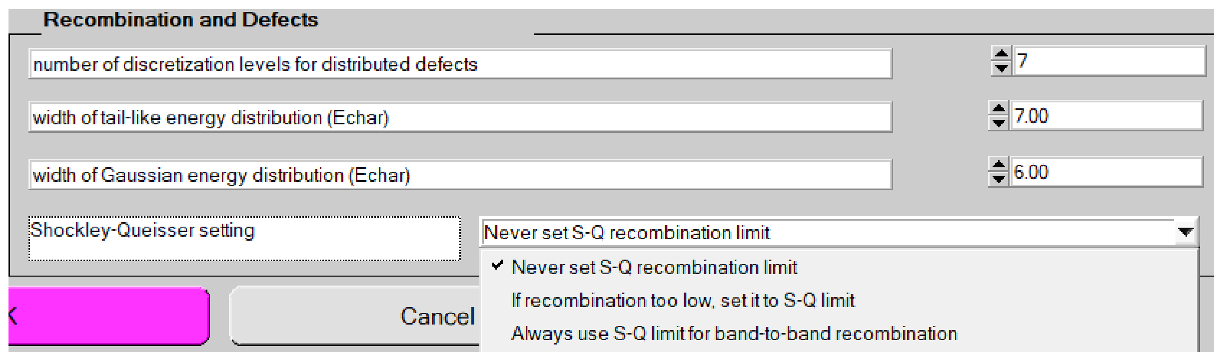

Fig. 2 Shockley-Queisser settings in the recombination block of the Numerical Panel in SCAPS.

When option 2 or 3 above are set, the S-Q checks are done for a layer, whenever one of the parameters d, E_g, N_C, N_V, C_r of that layer are changed (user interface, batch or script); and for the whole cell (all layers), when loading a new definition file (user interface, batch or script), when setting a S-Q mode in the Numerical Panel, and when leaving the Cell Definition Panel.

When a C_r value is replaced by its S-Q limit, the user is warned by a red color in the Layer Definition Panel, as shown in Fig. 3.

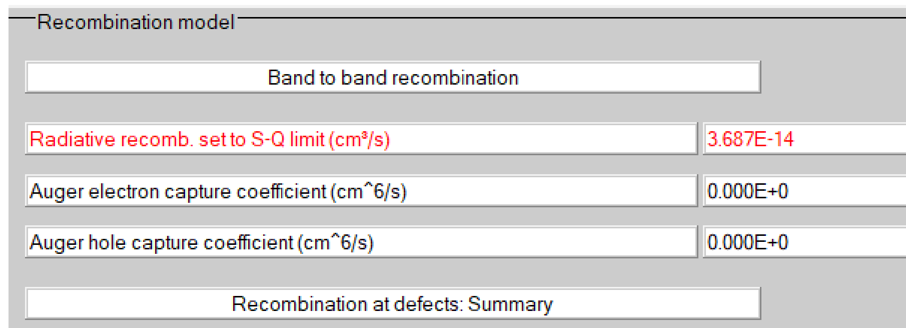

Fig. 3 Recombination Model block, top right in the Layer Definition Panel. When the user set value of Cr is replaced with the Shockley-Queisser limit according to Eq. (18), its new value, and the caption are highlighted in red.

The S-Q setting (never, if needed, or always) is saved in the definition file, if it was not the default setting ‘never’, and read and used when it is loaded. When a new definition file with a S-Q setting is loaded in an old SCAPS version < 3.3.11, it is of course not read, and no S-Q checks are done. When an old definition file is loaded in the new SCAPS >= 3.3.11, the default setting ‘never’ will be assumed.

Finally a warning when using ‘if needed’: when a C_r value was replaced with a calculated $C_{r,\text{S-Q}}$ limit, the original C_r is lost. When changing e.g. d in a batch setting, it is possible that a next S-Q check will leave the C_r value as it is, but that could be the S-Q limit set in the previous batch step, not the C_r value that the user originally has set. This happens when increasing d in a batch, that is equivalent to decreasing $C_{r,\text{S-Q}}$.

7. SCAPS simulation examples

7.1 Setting up a suitable def file to test

We start (of course) with `simple pn.def`, and do some changes:

- We set the recombination at the contacts to ‘as good as zero’: $S_n = 10^{-10}$ cm/s at the p-contact, and $S_p = 10^{-10}$ cm/s at the n-contact.
- We remove the defects in the p-layer and the n-layer, Then there is rigorously no SRH recombination
- We set the absorption model of both semiconductor layers to ‘step at E_g’, to mimic the situation of the original paper by Shockley and Queisser.
- For the absorber p-layer we set $\alpha_0 = 5\times10^5$ cm^{-1}; then the absorption depth is $1/\alpha = 0.02$ μm, thus (almost) all light will be absorbed in less then one μm; this can be considered as ‘sufficiently high’
- For the window n-layer we set $\alpha_0 = 10^{-5}$ cm^{-1}; then (almost) no light will be absorbed there, and the n-layer will act as a true window layer, even if its band gap is the same as E_g of the absorber, and not a good bit wider.
- We set the S-Q setting in the Numerical Panel to ‘always’
- This file is then saved as `simple pn S-Q.def`, and distributed with SCAPS 3.3.11

7.2 Simulating the ‘optimal efficiency graph’ $\eta_{\text{S-Q}}(E_g)$, and $V_{oc,\text{S-Q}}(E_g)$

The SCAPS simulation is shown, and compared with the literature table of [6], in Fig. 4. Note that in the SCAPS simulation, we did not set the default spectrum file *AM1.5G 1 sun.spe*, but *AM1.5G ed2 1 sun.spe*, that contains considerable more wavelength points (2002 wavelengths instead of only 120), and thus much better λ-resolution (and is a little bit slower…). We see that the Shockley-Queisser efficiency limit is quite well simulated by SCAPS: the SCAPS curve and the literature curve are as good as coinciding, only a very small deviation for narrow band gaps < 1 eV, where SCAPS underestimates the literature $\eta_{\text{S-Q}}$ with about 0.5 %. This is because SCAPS calculates a slightly lower J_{sc}, but more realistic than the very idealized Shockley-Queisser estimation of J_{sc}. The open circuit voltage V_{oc} of SCAPS and the literature coincide quite well, but for a systematic difference of 16 to 19 mV (SCAPS V_{oc} lower than literature V_{oc}). This is according to our expectations, see the discussion on the approximation of the integral in Eq. (15). We conclude that the SCAPS calculation of the Shockley-Queisser limit, that involves assumptions and approximations, performs quite well, and is usable in practice.

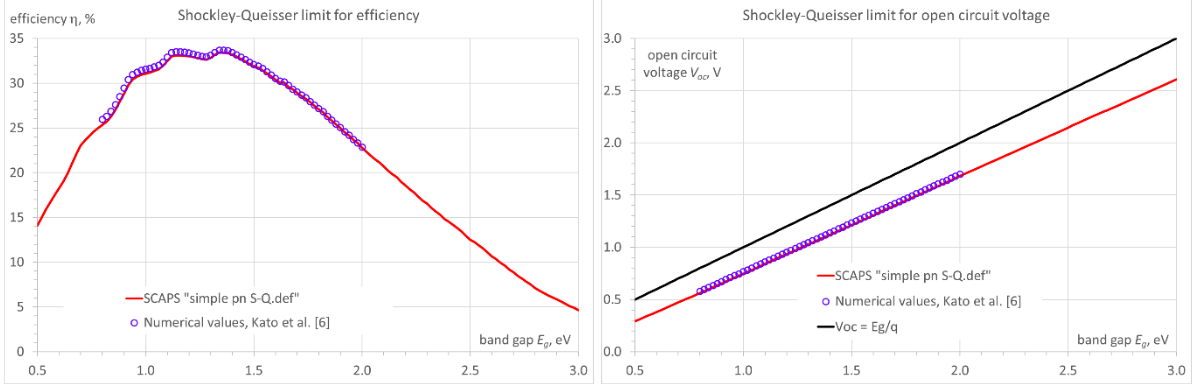

Fig. 4 Shockley-Queisser limits for efficiency η (left) and for open circuit voltage V_{oc} (right), as a function of band gap E_g. Red: simulated by SCAPS and Blue: as tabulated in literature [6]. In the $V_{oc}(E_g)$ plot (Right), the black line shows $V_{oc} = E_g/q$.

7.3 Illustration of SCAPS simulations with S-Q setting off or on

Let us now retake the simulation of Fig. 1, but with the two of the available S-Q settings: *never*, or *always*. We introduce one defect in each of the semiconductor layers of `simple pn S-Q.def`, thus the same defect for *p*-layer and *n*-layer; we use the default defect inserted by SCAPS when clicking 'add a defect' in the SCAPS Layer Definition Panel. We set up a batch/recorder simulation, where we simultaneously var the defect density N_t in the *p*-layer and in the *n*-layer, from 10^5 to 10^{15} cm^{-3}. The result is in Fig. 5.

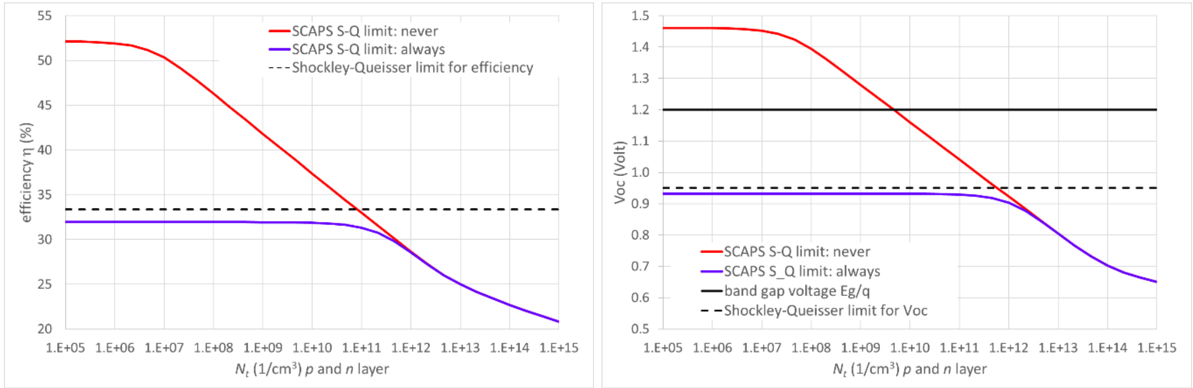

Fig. 5 Left: efficiency η and Right: open circuit voltage V_{oc} simulated by SCAPS for the problem file `simple pn S-Q.def`. The defect density N_t was varied simultaneously in the *p* layer and in the *n* layer, from extremely low (10^5 cm^{-3}) to rather high (10^{15} cm^{-3}), and the surface recombination at the contacts was set extremely low (S = 10^{-10} cm/s); radiative and Auger recombination were set at their default value of zero. Blue: with the SCAPS setting 'S-Q limit: always'. Red: with the SCAPS setting 'S-Q limit: never'. The Shockley-Queisser limits for efficiency η and for open circuit voltage V_{oc} are indicated, as well as the voltage corresponding to the band gap E_g = 1.2 eV of the *p* and *n* layer. With the setting 'S-Q limit: always', a 'Shockley-Queisser accident' does not occur!

This clearly illustrates that the setting 'S-Q limit: always' prevents a 'Shockley-Queisser accident' to occur when the defect density N_t is set (unrealistically) low.

7.4 The influence of layer thickness in the SCAPS implementation of S-Q

Look back to our essential result of Eq. (18), that we repeat here for the ease of reading:

$$C_{r,\,\text{S-Q}} = \frac{2\pi c}{N_V N_C}\left(\frac{kT}{hc}\right)^3\left(\frac{E_g}{kT}\right)^2 \cdot \frac{1}{d} \tag{18}$$

We already stated that we find it rather 'ugly' that a fundamental physical limit would (seemingly) depend on an easy-to-vary geometrical parameter – the layer thickness d. We should formulate this more precisely:

- It can be accepted that SCAPS replaces the actual material parameter C_r with the Shockley-Queisser limit $C_{r,\,\text{S-Q}}$ of Eq.(18), that depends on d.
- But it could not be accepted that the simulation result of a 'physical limit', that is, the *IV* curve, and, derived from it, the efficiency parameters η, V_{oc}, J_{sc}, *FF,* depend on d .

… so let us simulate and see what comes out in Fig. 6.

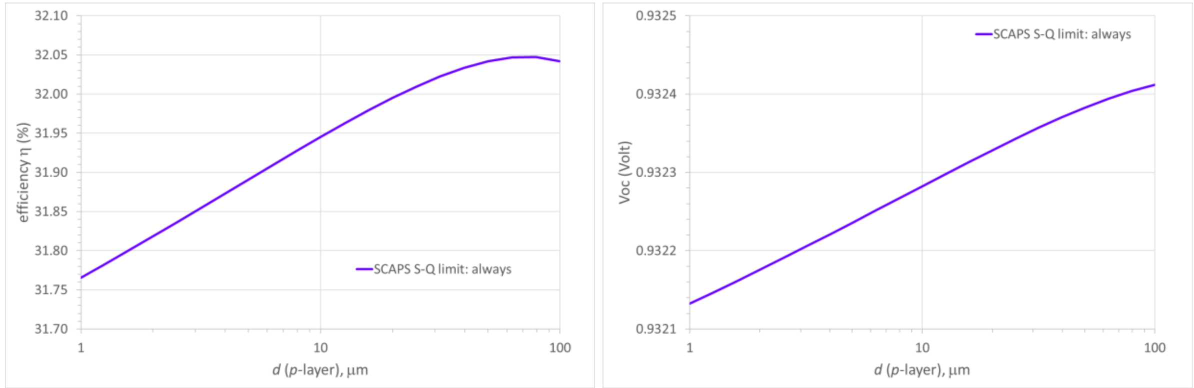

Fig. 6 Varying the p-layer thickness d in `simple pn S-Q.def` (with N_t = 10^5 cm^{-3}). The 'SCAPS S-Q limit: always' option is set. Left: efficiency η, and Right: V_{oc}.

First look to Fig. 6 Right, the $V_{oc}(d)$ simulation. The simulated V_{oc} in the Shockley-Queisser limit monotonically increases with increasing layer thickness d, what is not expected (or desired). But look to the scale: the $V_{oc}(d)$ variation, though clearly systematically, is very weak, V_{oc} varies over less than 0.3 mV over the thickness range 1 to 100 µm. We could conclude that, for practical purposes, the S-Q limit of V_{oc} is essentially independent of layer thickness. Bear in mind that even the best experimental cells have V_{oc} that is a few hundred (200 to 300) mV lower that the S-Q limit for V_{oc}, thus a variation of a few tenths of a mV is not of any practical relevance.

Then look to Fig. 6 Left, the η(d) simulation. The thickness dependence η(d) is more pronounced than the $V_{oc}(d)$ dependence: in the simulated d-range, η varies from 31.8 % to 32.05 % : that is somewhat less than 1 % relative (for $V_{oc}(d)$ it was less than 0.03 % relative). The higher sensitivity of η to thickness – compared to $V_{oc}(d)$ – should almost entirely be attributed to the thickness dependence of $J_{sc}(d)$: it varies from 38.90 to 39.39 $mAcm^{-2}$ over the

thickness range (not illustrated here), thus somewhat more than 1 % relative. Remember that the J_{sc} calculation (or estimation) of Shockley and Queisser was based on assumptions/abbreviations that were listed in page 4 of this document, the most important in this context being ‘the cell has infinite thickness’ or ‘is sufficiently thick’. These assumptions have nothing to do with physical limits or whatever, they were just there to make an quick estimate of J_{sc} in ‘ideal conditions’. SCAPS, in contrast, calculates J_{sc} taking all material parameters into account, including a finite layer thickness. Though we have set the material parameters of our simulated cell to be as good as possible ‘ideal’, a weak $J_{sc}(d)$ dependence is still manifest. Attribute that to the more realistic simulation of SCAPS compared to the very idealized estimation of Shockley and Queisser. The really weak thickness dependence of $V_{oc}(d)$ in the SCAPS simulation can be seen as a numerical evidence that our assumptions to implement the Shockley-Queisser limit, is valid.

8. SCAPS implementation of the Shockley-Queisser efficiency limit: summary

- The new SCAPS 3.3.11 (September 2023) implements the Shockley-Queisser limit for the efficiency and open circuit voltage of a solar cell.
- This S-Q limitation can turned off (default) or on.
- When turned on, the SCAPS S-Q limit implementation prevents ‘Shockley-Queisser accidents’.
- [however, the occurrence of a clear ‘Shockley-Queisser accident’ is an efficient warning to the user that the simulation parameters were not realistic, but far too idealistic!]

9. References

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[7] https://en.wikipedia.org/wiki/Shockley-Queisser_limit